# Studies on the electrochemical properties of copolymers of maleic acid, V : viscometric behaviors

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# STUDIES ON THE ELECTROCHEMICAL PROPERTIES OF COPOLYMERS OF MALEIC ACID, V

## Viscometric Behaviors

BY KAZUO MONOBE

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The viscosities of the maleic acid copolymers with styrene and vinyl acetate, which show electrochemically typical polydibasic characteristics, were studied mainly in aqueous medium and partly in acetone-water (1 : 1) mixture. The viscosity change due to the change in degree of neutralization at a given concentration reflected the polydibasic characteristics. The reduced viscosity as a function of concentration at a given degree of neutralization was studied at 25°C. Some data fitted Fuoss's equation for strong polyelectrolytes and some other did not fit. A general emipirical equation, $\frac{\eta_{sp}}{C}=\frac{A}{1-BC^n}+D$, was proposed for the viscometric data which did not fit Fuoss's equation. The values obtained for $n$ in the above equation were constant at a given degree of neutralization and for a given polymer, and all were intermediate between one-half and one. The significance of $n$ was discussed and the meanings of $A$ and $D$ in the above equation were also examined.

## Introduction

Electrochemically, we can readily understand[1] the polydibasic property by the two classes of dissociation based on the strong electrostatic interactions between the nearest neighboring charged groups on a polymer chain. However, the dissociation processes of polydibasic acids are apparently different from that of monomeric dibasic acids in the point that the counter-ions are subjected to the potential due to the clustering of ionic charges on the polymer molecule. In this paper, we will study the viscosity of the maleic acid copolymers which have a typical characteristic of polydibasic acid. We know well that the creation of electrostatic charges on a polymer molecule causes the expansion of its coil due to the intramolecular repulsion[2]. However, the solution viscosity of the maleic acid copolymers may depend on the coiling effect of non-solvating comonomer groups as well as on the uncoiling effect of charged groups in an aqueous medium[3]. The coiling force due to the nonpolar comonomer substituents may considerably influence on the coil configuration at low degree of ionization, while the uncoiling effect due to the increased net charges may be dominant at higher degree of ionization.

The viscometric behaviors of the 1 : 1 copolymer of maleic acid with either vinyl acetate

1) K. Monobe, *This Journal*, 30, 138 (1960)

2) See, for example, H. Eisenberg and R. M. Fuoss, *Modern Aspects of Electrochemistry*, Butterworth Sci. Pub., London, p. 29 (1954)

3) J. D. Ferry, D. C. Udy, F. C. Wu, G. E. Heckler and D. F. Fordyee, *J. Colloid Sci.*, 6, 429 (1951)

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(MA–VAc), or styrene (MA–S) are studied mainly in aqueous medium and partly in acetone-water (1 : 1) mixture. The viscosity measurements are restricted to the system which does not include external electrolytes, in the present investigation.

## Experimentals

The fractionated samples of the original 1 : 1 maleic anhydride copolymers described in the previous paper[1] were dissolved in conductivity water and used for viscosity measurements. The molecular weights of the maleic anhydride copolymers were determined by osmotic measurements[4] in tetrahydrofuran solutions. Based on those results, the molecular weight of the corresponding hydrolyzed maleic anhydride copolymers, MA–VAc and MA–S copolymers, were calculated as follows: 130,000 for MA–VAc–$F_3$, 100,000 for MA–S–$F_7$, 170,000 for MA–S–$F_5$, 200,000 for MA–S–$F_4$ and 240,000 for MA–S–$F_2$. The compositions were nearly 1 : 1 and details were described in Part III[5] of this series.

The solutions of those copolymers for viscosity measurements were diluted with water (or with acetone and acetone-water mixture) from the stock solutions of about 0.4 g/dl. The viscosities of the solutions were measured at the concentrations below 0.2 g per 100 cc in Ostwald viscosimeters at 25.0±0.1°C. The flow time for water and for acetone-water (1 : 1 in weight) mixture[6] was 58.6 sec and 82.3 sec respectively at 25°C. The kinetic energy corrections of solution viscosities were neglected here. The concentrations of the maleic acid copolymers, which were represented by grams per 100 cc, were calculated from the weights of the original anhydride copolymers used, their free carboxyl contents, monomer compositions in the copolymers and the concentrations of equivalent alkali. The degree of neutralization $\alpha$ was defined here in the way that $\alpha=1$ and $\alpha=0.5$ represent the neutralization point and the half neutralization point, respectively.

## Results and Discussion

**1 Viscosity change due to the degree of neutralization** We shall show at first the viscosity change due to the degree of neutralization. Fig. 1–I gives the plots of the reduced viscosity, $\frac{\eta_{sp}}{C}$, at constant concentration $C$, against the degree of neutralization $\alpha$ in aqueous medium. Fig. 1–II shows the same viscometric plots in acetone-water solution. In Fig. 1–I, curves $A_1$, $A_2$ and $A_3$ are the $\frac{\eta_{sp}}{C}\sim\alpha$ curves for MA–VAc copolymer $F_3$ whose molecular weight is 130,000, at the concentrations of 0.19, 0.10 and 0.04 g/dl, respectively. $B_1$, $B_2$ and $B_3$ are the curves for MA–S copolymer $F_7$ whose molecular weight is 100,000 at the same concentrations as that for MA–VAc copolymer.

4) K. Monobe, *to be published*
5) K. Monobe, *This Journal*, 30, 155 (1960)
6) The dielectric constant is 48.2 at 25°C. *Landolt-Börnstein Tab.*, Erg. IV

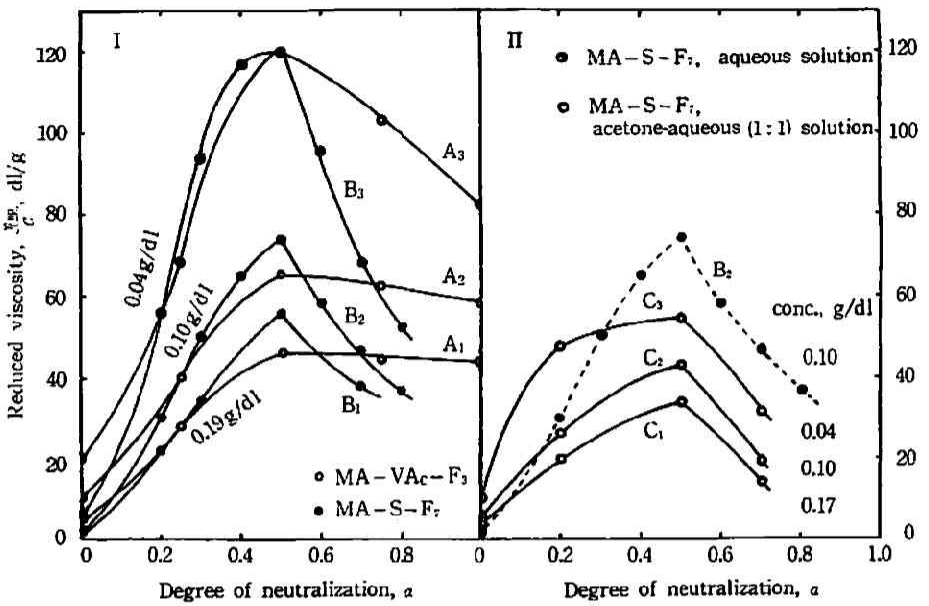


Fig. 1 Viscosity change at 25°C plotted against degree of neutralization with sodium hydroxide

I: aqueous solution

| conc. (g/dl) | 0.19 | 0.10 | 0.04 |
|---|---|---|---|
| MA-VAc (○) | $A_1$ | $A_2$ | $A_3$ |
| MA-S (●) | $B_1$ | $B_2$ | $B_3$ |

II: acetone-aqueous (1 : 1) solution

| conc. (g/dl) | 0.17 | 0.10 | 0.04 |
|---|---|---|---|
| MA-S (○) | $C_1$ | $C_2$ | $C_3$ |

As shown in Fig. 1–I, the reduced viscosity at each constant concentration shows the maximum value at $\alpha=0.5$ for the two copolymers. In particular, MA–S copolymer exhibits a sharp decrease in $\frac{\eta_{sp}}{C}$ at $\alpha>0.5$. The sharp increases of the reduced viscosities with increasing $\alpha$ up to 0.5 for the two copolymers are based on the increased net changes. When $\alpha$ increases beyond 0.5, the counter-ions binding due to the nearest neighboring interaction becomes so dominant that the reduced viscosities decrease. In the styrene copolymer, the counter-ions effect based on the hydrolysis causes particularly a sharp decrease of reduced viscosity. The hydrolysis results from the stronger nearest neighboring interaction[1]. Thus, the viscosity results reflect a polydibasic characteristic.

In Fig. 1–I, the reduced viscosities for the styrene copolymer are distinctly smaller than those for the vinyl acetate copolymer at low degree of neutralization ($\alpha<0.2$). However, the reduced viscosities at $0.2<\alpha<0.5$ are a little larger, in spite of the lower molecular weight. Now attention will be directed here on the reduced viscosities near the degree of dissociation where the average dissociation constants, $pK_1$ and $pK_2$, have been evaluated for the two copolymers. For an example, at the concentration of 0.19g per 100cc which corresponds to nearly 0.01 monomole per liter, we have the values of $\frac{\eta_{sp}}{C}=28$ at $\alpha=0.25$ and $\frac{\eta_{sp}}{C}=35$ at $\alpha=0.75$ for MA–S copolymer. The corresponding values for MA–VAc copolymer are 28 and 44 at $\alpha=0.25$ and $\alpha=0.75$ respectively. These values are considerably higher than the values at $\alpha=0$ (1.6 for MA–S and 5 for MA–VAc) and than the intrinsic viscosities[5] of the uncharged copolymer

anhydrides in organic medium. We shall assume that the reduced viscosity measures the size of the solute in polyelectrolyte solutions as well. Thus, we can expect a considerable expansion of polymer coil for the two copolymers at $\alpha=0.25$ or $\alpha=0.75$. The relatively lower value at $\alpha=0.75$ for MA–S copolymer may be based on the counter-ions effect due to the hydrolysis rather than on the coiling effect due to the cohesive force of phenyl groups, judging from the fact that the same value of reduced viscosity as that for MA–VAc copolymer at $\alpha=0.25$ can be obtained. It is a problem on the domain where the electrostatic force is predominant. However, we may expect a tighter coiling at $\alpha<0.2$ for MA–S copolymer as pointed out by Ferry[5].

**2 Reduced viscosity as a function of concentration** The aqueous solutions of the maleic acid copolymers at various degrees of neutralization (the stock solutions of about 0.4 g/dl) were diluted with water and the viscosity of the solutions were measured at 25°C. Fig. 2 shows the viscosity curves, $\frac{\eta_{sp}}{C}=f_\alpha(C)$, which represent the reduced viscosity as a function of concentration at the constant degree of neutralization.

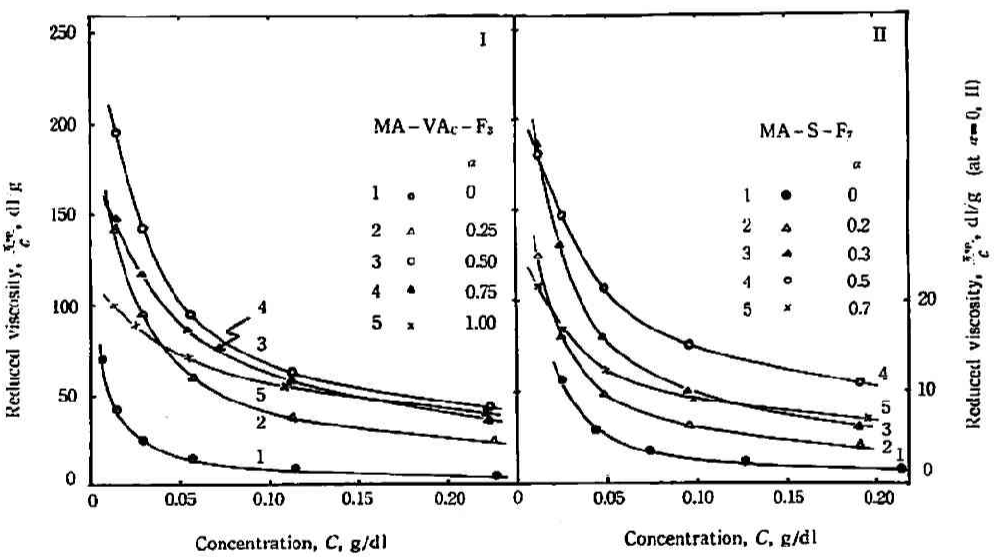


Fig. 2 Reduced viscosity as a function of concentration at 25°C

I: MA-VAc copolymer aqueous solutions

| curve | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| sign | ● | △ | ○ | ▲ | × |
| α | 0 | 0.25 | 0.50 | 0.75 | 1.00 |

II: MA-S copolymer aqueous solutions

| curve | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| sign | ● | △ | ▲ | ○ | × |
| α | 0 | 0.2 | 0.3 | 0.5 | 0.7 |

As is obvious in Fig. 2, general polyelectrolyte behavior[7] that the reduced viscosity increases with dilution, presents itself markedly. However, when we look over the curves in detail, we can notice that the increasing rate of reduced viscosity on dilution varies according to the degree of neutralization; the higher the degree of neutralization is, the smaller the slope of curve is. The results for MA–VAc copolymer shown in Fig. 2–I and also for MA–S copolymer in Fig.

7) R. M. Fuoss and U. P. Strauss, *J. Polymer Sci.*, 3, 246 (1948)

2-II give a similar tendency.

In general, the reduced viscosity of strong polyelectrolytes is described quantitatively by the equation of Fuoss[8].

$$\frac{\eta_{sp}}{C}=\frac{A}{1+BC^{\frac{1}{2}}}+D, \qquad (1)$$

where $A$, $B$ and $D$ are the characteristic constants and $C$ is the polymer concentration. However, when we plot the results in Fig. 2 according to Equation (1) in reciprocal form, some unreasonable plots are obtained, with which the extrapolations to $C=0$ give the negative values[9]. The reasonable plots are obtained at $\alpha\geq 0.5$ for MA-S and at $\alpha=1$ for MA-VAc except the results in extremely high dilution. The other cases show the unreasonable plots. At first, we shall show some examples which fit well to Equation (1). Fig. 3 gives the linear relationship between $\left(\frac{\eta_{sp}}{C}-D\right)^{-1}$ and $C^{\frac{1}{2}}$ for MA-S. Table 1 gives the constants. $A$, $B$ and $D$ according to Equation (1).

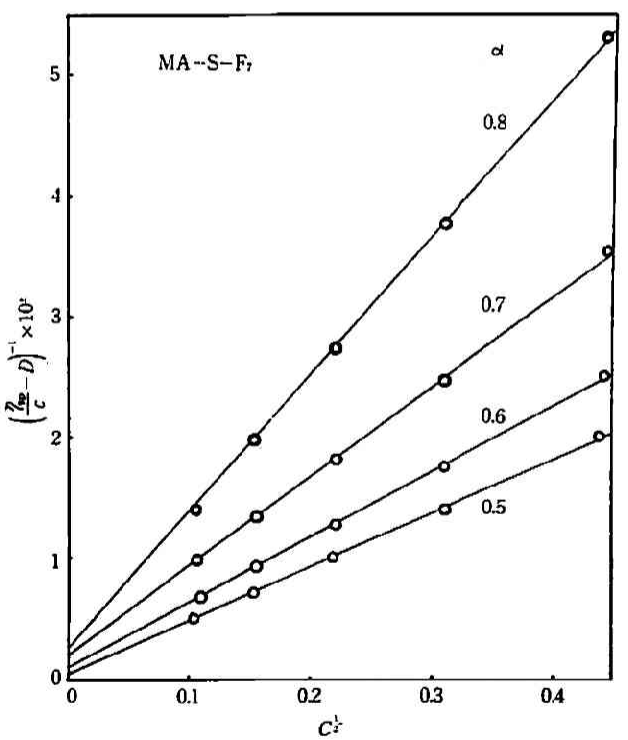


Fig. 3 Plots of $\left(\frac{\eta_{sp}}{C}-D\right)^{-1}$ against $C^{\frac{1}{2}}$ for MA-S-F$_7$ at $\alpha\geq 0.5$

Since the intercepts of the ordinate at $C=0$ in Fig. 3 were very small, we obtained the values of $A$ and $B$ in Table 1 by means of an alternative method[8]; plotting $\left[\left(\frac{\eta_{sp}}{C}-D\right)C^{\frac{1}{2}}\right]^{-1}$ against $C^{-\frac{1}{2}}$ and the slope and intercept were used to evaluate $A$ and $B$, respectively. These $A$ values

8) R. M. Fuoss and G. I. Cathers, *J. Polymer Sci.*, 4, 97 (1949)
9) J. R. Schaefgen and C. F. Trivisonno, *J. Am. Chem. Soc.*, 74, 2715 (1952)

Table 1 Characteristic constants for MA–S copolymer $F_7$ according to Equation (1)

| $\alpha$ | $A$ | $B$ | $D$ |
|---|---|---|---|
| 0.5 | 1200 | 60 | 6 |
| 0.6 | 1000 | 54 | 4 |
| 0.7 | 700 | 55 | 9 |
| 0.8 | 500 | 58 | 12 |

are considerably large in spite of the influence of hydrolysis[1] at $\alpha > 0.5$, where $A$ corresponds to the intrinsic viscosity of the highly stretched polymer. The other results in higher molecular weight sample (MA-S-$F_2$) showed far larger values of $A$.

However, we can observe the decrease[10] of the reduced viscosity at extremely low concentration where the relative viscosity is still high. The result for MA–S copolymer $F_7$ is shown in Fig. 4, where the concentration range measured is from $2.5\times10^{-2}$ to $0.25\times10^{-2}$ g per dl. Although the concentration is extremely low, the relative viscosity obtained is ranging from about 4.5 to about 1.4. We could observe more distinctly the same tendency in the high molecular weight sample (MA–S–$F_2$) as that shown in Fig. 4, but we reserved the data because of too high viscosities.

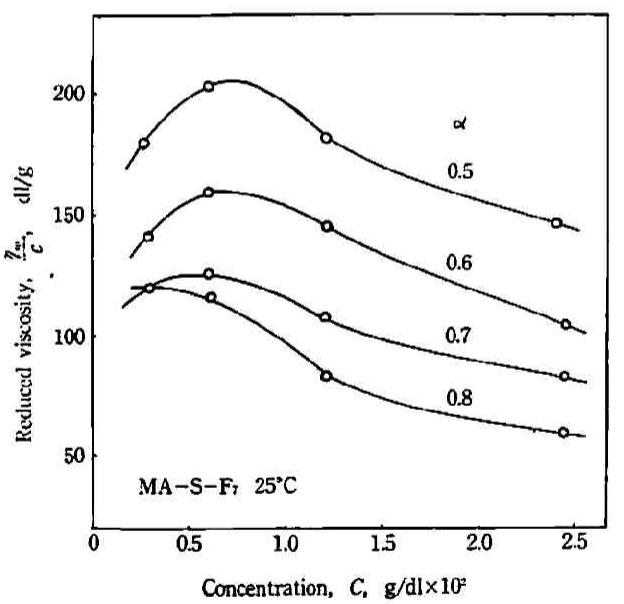


Fig. 4 Reduced viscosity of MA–S–$F_7$ in extremely dilute solution at 25°C

We may point out here that the maximum values of the reduced viscosities for MA–S copolymer $F_7$ shown in Fig. 4 may be still larger than the corresponding value for polymethacrylic acid; Oth and Doty[11] have shown the value of $A=55.5$ at $\alpha=0.68$ for polymethacrylic acid

10) J. A. V. Butler, A. B. Robins and K. V. Shooter, *Proc. Roy. Soc.*, A241, 299 (1957)
K. Hotta, *Chem. High Polymers* (Tokyo), 12, 276 (1955)
11) A. Oth and P. Doty, *J. Phys. Chem.*, 56, 43 (1952)

whose molecular weight is 90,300.

Now we shall treat quantitatively the data, which give no reasonable plots by Equation (1), in the following way. The viscosity behavior of weak polyelectrolytes on dilution can be described generally by the equation of Kern[12];

$$\frac{\eta_{sp}}{C}=KC^{n'}, \tag{2}$$

where $K$ and $n'$ are constants. We can modify Equation (2) in the analogous form with Equation (1) as follows;

$$\frac{\eta_{sp}}{C}=\frac{A}{1+BC^{n}}+D. \tag{3}$$

In Equation (3), if we neglect the consatnt $D$ and set $n=-n'$ and $\frac{A}{B}=K$, then Equation (3) is reduced to Equation (2), when the term $BC^n$ is much larger than 1. On the other hand, Schaefgen[9] has proposed the following equation applicable[13] to certain polyamides of low charge density;

$$\frac{\eta_{sp}}{C}=\frac{A}{1+BC}+D. \tag{4}$$

The term which is proportional to $C$ is introduced in Equation (4) in place of $BC^{\frac{1}{2}}$ in Equation (1), as the factor[7] which relates to the interaction between polyion and its counter-ions.

Thus, Equation (3) may be regarded as a general form of Equations (1) and (4). We applied Equation (3) to the viscometric data which were not explained by Equation (1). At first the evaluations of $n$ and $D$ in Equation (3) were done for viscometric data of the maleic acid copolymers.

The evaluation of the exponent $n$ is made as follows; first, an approximate value of $n$ can be estimated by plotting $\log\left(\frac{\eta_{sp}}{C}\right)^{-1}$ against $\log C$. Using the $n$ value obtained, $D$ is estimated by plotting $\frac{\eta_{sp}}{C}$ against $C^{-n}$. Secondly, the value of $n$ is re-estimated by plotting $\log\left(\frac{\eta_{sp}}{C}-D\right)^{-1}$ against $\log C$, using the $D$ value obtained above. Using the re-estimated $n$ value, the value of $D$ is newly estimated. The final values of $n$ and $D$ can be determined after repeating this procedure twice or thrice. Thus, the linear relationship between $\left(\frac{\eta_{sp}}{C}-D\right)^{-1}$ and $C^n$ may be obtained using the final values of $n$ and $D$.

Fig. 5 shows some the log-log plots used in order to evaluate $n$ for the maleic acid copolymers at $\alpha=0$ (I) and at $\alpha>0$ (II) in the aqueous solutions, and in the acetone-water (1 : 1) solutions (III). The values of $n$ are obtained from the slopes of the straight lines.

12) W. Kern, *Z. phys. Chem.*, **181A**, 249 (1938)

13) (a) Application of Eq. (4) to 14 different polyelectrolytes has been reported by R. H. Wiley and co-workers (*J. Am. Chem. Soc.*, **76**, 720 (1954), *C. A.*, **49**, 7972 (1955)). These authors evaluated the values of $K$ and $n'$ in Eq. (2) from the $\log\frac{\eta_{sp}}{C}-\log C$ plots of their viscometric data and pointed out that the constant $K$ of Eq. (2) was equal to 1.34 times the constant $D$ of Eq. (4). (b) As for $n'$, they obtained the values, $n'=-0.324\sim-0.380$ for potassium *p*-vinylbenzene sulfonate polymers which were relatively low viscosities and were studied in the concentration range of about 1.0~0.1 g/dl.

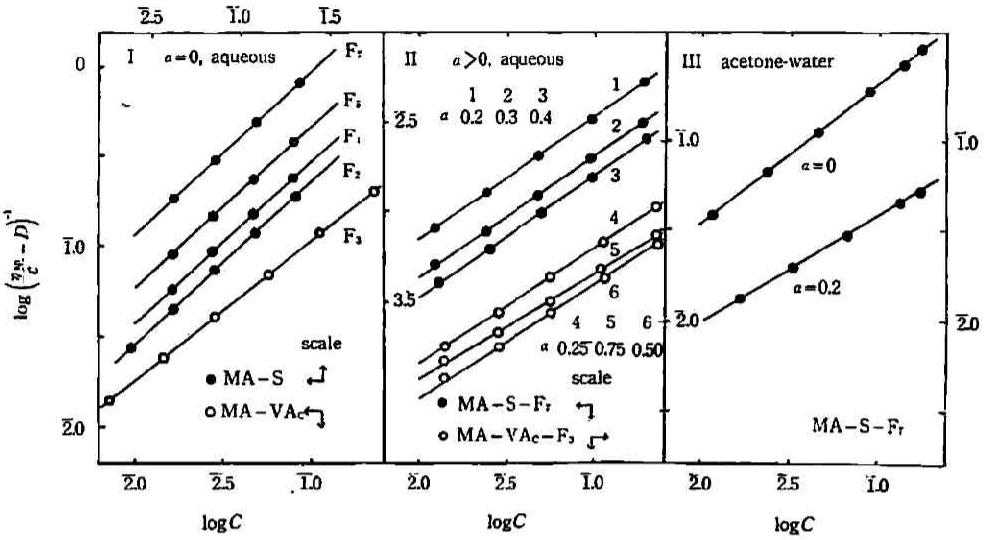


Fig. 5 Evaluation of $n$ in Equation (3) for the copolymers of maleic acid
I: at $\alpha=0$ in aqueous solutions, II: at $\alpha>0$ in aqueous solutions,
III: in acetone-aqueous (1 : 1) solutions

The values obtained for $n$ are summarized in Table 2.

Table 2 The values of $n$ and $D$ in Equation (3) for the copolymers of maleic acid*

| | MA-S copolymer | | | | | | | | MA-VAc copolymer | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $F_7$ | | $F_5$ | | $F_4$ | | $F_2$ | | $F_3$ | | |
| $\alpha$ | $n$ | $D$ | $n$ | $D$ | $n$ | $D$ | $n$ | $D$ | $n$ | $D$ | $\alpha$ |
| 0 | 0.90 | 0.5 | 0.90 | 0.8 | 0.90 | 0.9 | 0.90 | 1.0 | 0.78 | 1.0 | 0 |
| 0.2 | 0.68 | 2.0 | | | | | 0.68 | 2.0 | 0.63 | 1.0 | 0.25 |
| 0.3 | 0.68 | 3.0 | | | | | 0.54 | 6.0 | 0.63 | 3.5 | 0.5 |
| 0.4 | 0.68 | 6.0 | | | | | 0.54 | 12.0 | 0.58 | 2.0 | 0.75 |
| $[\eta]^{**}_{T.H.F.}$ | | 1.00 | | 1.70 | | 1.95 | | 2.35 | | 0.70 | |

* see Fig. 5

** The intrinsic viscosity of the original maleic anhydride copolymers in tetrahydrofuran solutions at 20°C.
The values, $n=0.76$ at $\alpha=0$ and $n=0.58$ at $\alpha=0.2$, for MA-S-$F_7$ in acetone-water (1 : 1) solution have been obtained also from Fig. 5-III.

All values for $n$ in Table 2 are intermediate between one-half and one[10].

A fact that the viscosity for the copolymers of maleic acid shows the dependence on concentration intermediate between one-half and one according to Equation (3) has a very interesting

14) The result of R. H. Wiley and co-workers (Reference 13 (b)) shows that the constant $n$ according to Eq. (3) is $n<0.5$ for potassium $p$-vinylbenzene sulfonate polymers in the concentration range studied, since the value of $n'$ in Eq. (2) is roughly equal to the value of $n$ in Eq. (3) although their treatment (Eq. (4) and Eq. (2)) differs from our treatment (Eq. (3)). On that point, we shall discuss in other place.

meaning in relation to Schaefgen's suggestion[15] given in his paper. We shall consider this meaning later.

The values obtained for the constant $D$ are also shown in Table 2. $D$ corresponds to the intrinsic viscosity of the fully screened polymer. In order to compare it with the uncharged copolymer, we show in Table 2, the intrinsic viscosities of the maleic anhydride copolymers in tetrahydrofuran solutions. We may roughly expect the tighter coiling of MA–S copolymer at $\alpha=0$ in aqueous medium from the comparison.

We evaluate subsequently the constants $A$ and $B$ in Equation (3). The linear relationship between $\left(\frac{\eta_{sp}}{C}-D\right)^{-1}$ and $C^{a}$ for the copolymers of maleic acid can be obtained as shown in Fig. 6.

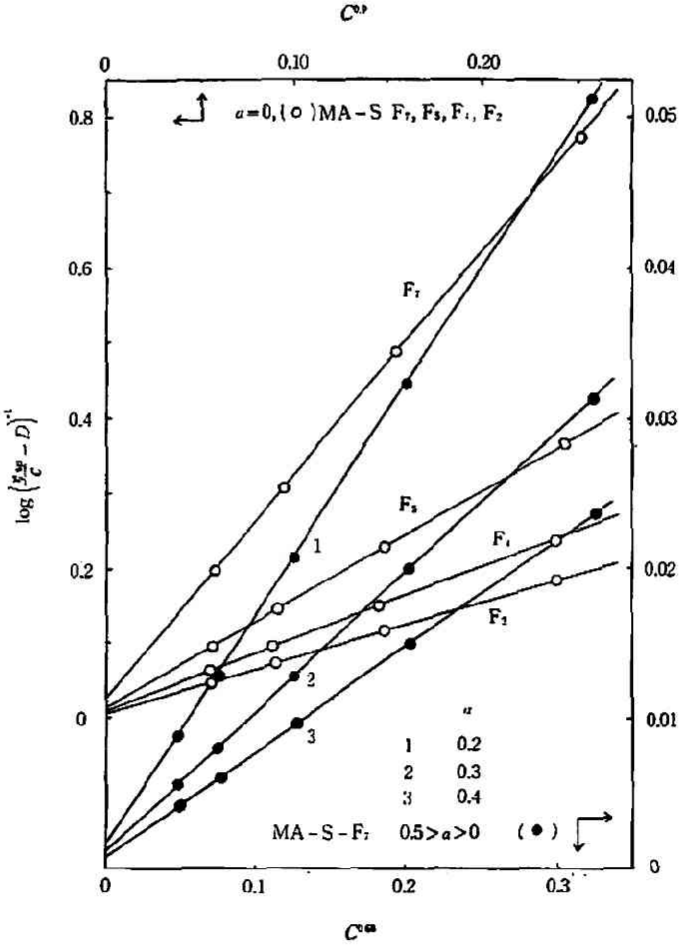


Fig. 6 Plots of $\left(\frac{\eta_{sp}}{C}-D\right)^{-1}$ against $C^{a}$ for MA-S according to Equation (3)

Plot of each fraction of MA-S, $F_7$, $F_5$, $F_4$ and $F_2$ at $\alpha=0$ is shown by open circle (○). Plot of MA-S-$F_7$ at $0.5>\alpha>0$ is shown by filled circle (●).

15) Reference 9, footnote (9)

Table 3 gives the values of $A$ and $B$ which are evaluated from the slope and intercept of the straight lines in Fig. 6 and which can be also evaluated by plotting $\left[\left(\frac{\eta_{sp}}{C}-D\right)C^n\right]^{-1}$ against $C^{-n}$.

Table 3 The values of $A$, $B$ and $D$ in Equation (3)
(MA–S, at $\alpha=0$ in aqueous medium)

| | MA–S copolymer | | | |
|---|---|---|---|---|
| | $F_2$ | $F_4$ | $F_5$ | $F_7$ |
| $A$ | 133 | 100 | 71 | 37 |
| $B$ | 93 | 96 | 102 | 108 |
| $D$ | 1.0 | 0.9 | 0.8 | 0.5 |

Now we shall consider at first on the term $BC^n$ in Equation (3), where $n$ holds the relation, $0.5<n<1$. Generally, an increase of reduced viscosity on dilution in polyelectrolytes is based on an increase of the net charges on a polymer molecule. On the other hand, the molecular shape is the result of the operation of electrostatic repulsion and nonelectrostatic contractility. When charge density is high, the intramolecular electrostatic repulsion between the net charges will become dominant. However, when the charge density is low, the effect of polymer-solvent interaction will be marked[15]. At a low degree of neutralization in the aqueous solutions of maleic acid copolymers, the interaction between the non-solvating comonomer substituents and water may be considerably strong, particularly in MA–S copolymer[3]. Thus, our viscometric data for the copolymers of maleic acid obey Equation (3) which holds the relation, $0.5<n<1$. Katchalsky[16] has proposed a viscosity function of the following form based on a theoretical standpoint,

$$\frac{\eta_{sp}}{C}=\frac{A}{1+BC^{\frac{1}{2}}+B'C}+D. \qquad (5)$$

Equation (3) which holds the relation, $0.5<n<1$, may be regarded as an empirical equation of Equation (5). On the other hand, if we survey the exponent $n$ on the increasing rate of the reduced viscosity with dilution in our present data, then we know that the larger the increasing rate is, the larger the value of $n$ becomes. This behavior may correspond to that the degree of dissociation increases on dilution at a given degree of neutralization. Thus, we may have another aspect of Equation (3) that the increase in the number of dissociated groups in addition to the expansion of the ionic atmosphere surrounding the ionized group on a polymer molecule with dilution, results the more increase of the net charge.

Next we shall test the values of $A$ shown in Table 3 by the equation,

$$[\eta]=kM_n^a. \qquad (6)$$

$A$ corresponds to the intrinsic viscosity $[\eta]$ of the fully stretched polymer. Fig. 7 shows a relation between $\log A$ and $\log M_n$ for MA–S copolymer at $\alpha=0$. The value obtained for $a$ is 1.3

16) A. Katchalsky, *J. Polymer Sci.*, 12, 159 (1954)

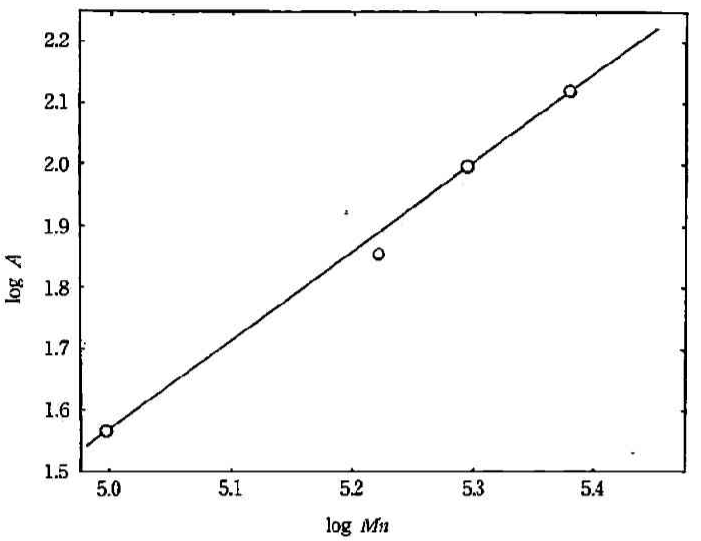


Fig. 7 Relation between $\log A$ and $\log Mn$ for MA–S copolymer

which means considerable expansion of the polymer coil. However, the values of $A$ for the copolymer at $\alpha>0$ are very large and the decrease of the reduced viscosity is observed experimentally on extremely high dilution, where $A$ in Equation (3) may have only a hypothetical meaning but $n$ in Equation (3) may not lose the significance mentioned above.

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